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Plasma synthesis of hexagonal-pyramidal graphite hillocks

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ABSTRACT

We report on the synthesis and natural occurrence of hexagonal-pyramidal graphite hillocks on graphite crystal substrates. Synthetic hillocks were obtained from flexible graphite sheets and highly oriented pyrolytic graphite via argon plasma etching in a standard helicon configuration reactor. High-resolution transmission electron microscopy and electron diffraction suggest these hillocks have a high degree of perfection. Their size distribution ranges from 50 to 800 nm across and up to 1 μm along the c-axis. As a reference, natural crystals from Tanzania exhibiting the same morphology are presented. Also, a formation mechanism of the plasma-synthesized structures by an etching process is detailed. This new type of vertically aligned carbon nano- and microstructures presents a peculiar geometry including nano-arches at the graphite edge planes which induce a strong resistance to the plasma etching.

1. Introduction

Due to its versatile hybridization, carbon occurs as many different allotropic forms. One in particular, graphite, exhibits a remarkable variety of geometrical forms [1] such as flakes [2], dendrites [3], whiskers [4], cones [5–7], onions [8–10], spheres [11–14] and polyhedral crystals [15–17]. As is well known, graphite is the three-dimensional stacking of two-dimensional honeycomb lattices known as graphene [18]. In micro- and nanocones, the graphene sheets may be organized around a nanotube core in a so-called tubular configuration [19]. Quite the opposite, a platelet nanocone exhibits a graphene stacking perpendicular to the c-axis of the cone [20]. The graphite polyhedral crystals discovered by Gogotsi et al. [15] present a polygonalized tubular configuration. The hexagonal-pyramidal graphite hillocks (HPGHs) of this study may be seen as their stacked platelet counterparts. These structures belong to the wide family of the vertically aligned nanostructures (VANs) which present unique mechanical, electrical and thermal properties not seen in the bulk graphite and thus suggest themselves for various applications from field-emission devices to gene drug delivery and DNA analytes detectors [21–23]. The high-purity and high stability of the graphite hillocks in this study could be a strong asset for potential applications.

Rare but similar graphite hillocks on graphite crystals from several geological occurrences are also briefly described. HPGHs have already been observed in natural graphite from the Chernorudka–Barakchin Fault Zone, Western Baikal Region, Russia [24,25], but detailed analyses of their

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structures have so far not been presented. We have found that HPGHs also occur on the surface of some natural graphite crystals from the Broken Hill mine, Australia, on graphite crystals found in fluorite from the Kimwarer ore body, Kerio Valley, Kenya and most significantly, on high quality graphite crystals enclosed in nearly pure dolomite from an occurrence near Moshi, Tanzania. Although they are extremely rare by comparison with world-wide graphite occurrences, the graphite crystals with associated HPGHs from the Moshi occurrence are relatively abundant and make further studies of their structure possible.

This work is devoted to the synthesis of HPGHs from flexible graphite (FG) and highly oriented pyrolytic graphite (HOPG) via argon plasma etching. Their structure is analyzed via electron microscopy. Natural graphite hillocks from Moshi are also presented as they exhibit similar morphology and crystallographic properties. The evolution of the plasma-synthetized hillocks lead to a suggested formation mechanism detailed in the discussion.

2. Experiment

2.1. Experimental set-up

Plasma-synthesized HPGHs were produced from $2 \times 2\ cm^2$ samples of 125-μm thick FG foils, which essentially consist of compressed exfoliated graphite flakes of up to a couple micrometers in thickness and less than 10 μm in diameter (Fig. 1A). The surface thus presents a high density of topographical defects as reflected by the mosaic spread which is $(3.5 \pm 1.5)°$, the domain size 30–40 nm and the density close to $1.2\ g\ cm^{-3}$. The carbon purity of 99.8% has been confirmed via energy dispersive X-ray spectroscopy (EDS) at 30 kV; the flexible graphite contains traces of Si and P (Fig. S1 of the supplementary data). Other elements can be present but were usually under the EDS detection limit. Additional plasma treatments have been performed on $1 \times 1 \times 0.2\text{-}cm^3$ HOPG of 99.99% carbon purity whose mosaic spread is $(0.8 \pm 0.2)°$, domain size less than 10 μm and a density of $2.26\ g\ cm^{-3}$. The HOPG is exfoliated with adhesive tape before plasma treatment. This leads to local topographical imperfections such as steps and suspended graphite foils. Both types of graphite were provided by Goodfellow SARL.

During the plasma treatment, the graphite lies on a substrate-holder at floating potential in the center of a standard helicon configuration reactor with an radiofrequency (rf) Boswell-type antenna at 13.56 MHz [26,27]. Prior to (and during) the plasma treatment, the substrate-holder is heated to 650 °C to desorb the oxygen and water previously adsorbed by the sample. This is an important process to ensure the purity of the Ar gas phase since hydrogen and oxygen lead to plasma-assisted chemical erosion processes. Surface temperature is monitored by a type-K thermocouple whose hot junction is located under the substrate-holder surface. Then, argon (99.9999% purity) is injected into the reactor at a flow rate of 20 sccm and the graphite undergoes rf plasma treatment at 1800 W with a pressure of 1.3 Pa in the rf wave coupling mode. Due to the reactor geometry as well as limitations in rf power (2 kW) and axial magnetic field (0.02 T), the wave coupling mode transfers the injected power to the discharge via both helicon and Trivelpiece–Gould waves [28–30]. The former generate a high-density plasma column ($n_e = 10^{12}$–$10^{13}\ cm^{-3}$) impinging upon the sample while the latter generate a low-density peripheral plasma shaped as a hollow cylinder ($n_e = 10^{10}$–$10^{11}\ cm^{-3}$) around the substrate-holder (Fig. 1B). To ensure only traces of oxygen and hydrogen are to be found, the content of such species is monitored during the plasma treatment by optical emission spectroscopy, using an Avantes AvaSpec-2048 spectrometer.

Natural samples were found in a deposit of otherwise pure, pale blue dolomite located southwest of Moshi, in the Kilimanjaro region of northern Tanzania. The occurrence is a small open pit excavation whose geology, to our knowledge has not been systematically studied. This occurrence's graphite hillocks are located on the surfaces of flat well-crystallized graphite crystal hosts that ranges from 0.1 to 6 mm across and which can be easily exposed from the enclosing dolomite by dissolving the latter in hot dilute (10%) HCl.

Structure modifications were observed using a Hitachi S-4700 field emission scanning electron microscope (SEM) for the natural crystals and a Hitachi S-4800 and an FEI XL30-SFEG SEMs for the synthetic ones. The HPGHs can also be transferred to transmission electron microscopy (TEM) grids, with holey or continuous carbon films, using simple mechanical cleavage by rubbing the grid over the substrate. This process is less efficient for the natural samples due to the small size of the latter. After transfer, selected area electron diffraction (SAED) and TEM imaging were performed in an FEI CM200 operated at 200 kV and high-resolution transmission electron microscopy (HRTEM) imaging in an aberration-corrected JEM-ARM200F microscope from JEOL operated at 80 kV. EDS have been performed in the FEI SEM for global spectra and in the JEOL TEM for nanoscale analyses.

2.2. Plasma treatment with low-energy ions

Due to the high mobility of the electrons, the surface of any object (e.g. graphite substrate) immersed in a plasma is negatively charged compared to the latter. This potential difference between the plasma (V_p) and the sample surface (V_f, the floating potential) is limited to a region close to the surface called the sheath. It permits the maintenance of equal ion and electron fluxes upon the substrate by containing the electrons in the plasma and by accelerating the ions towards the surface. Energetic ions transfer kinetic energy to the graphite lattice and, at such low pressure, hit the surface at normal incidence with an energy (V_p–V_f).

The plasma and floating potentials were measured by means of a Smartprobe rf compensated Langmuir Probe from Scientific Systems Ltd. The results show that the argon ions energy is about 25 eV, well below the sputtering threshold of argon on graphite, which is around 56.3 eV [31]. Besides, the sputtering of graphite is usually carried out in magnetron physical vapor deposition processing at 200 eV and greater. However, the samples suffer a substantial mass loss after plasma treatment leading to an etching rate close to $1\ \mu m\ h^{-1}$ without substrate polarization.

A multi-step process, known as ion-irradiation-induced damage (I3D), which is extensively described in the reviews

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